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Catalytic dehydration of methanol to dimethyl ether (DME) over solid-acid catalysts

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Abstract

A series of solid-acid catalysts with different components contents were prepared by coprecipitation (sol–gel) method. These samples comprised γ-alumina and modified γ-Al_2O_3 with silica. The effects of silica various contents have been investigated on purpose to determine an optimum one. Dehydration of methanol to dimethyl ether (DME) on solid-acid catalysts was studied in a fixed-bed flow reactor at a temperature of 300 °C under atmospheric pressure and a GHSV of 15,600 h^{-1}. The catalysts have been characterized using BET, TGA, XRD, NH_3–TPD and elemental analysis techniques and also the results are reported. According to the experimental results, the pure γ-Al_2O_3 catalyst shown a good catalytic activity, but this sample undergoes a fairly rapid and irreversible deactivation. Silica-modified catalysts have shown better performance compared to the untreated γ-Al_2O_3. It was found that surface areas increase with increasing in the silica loading at aluminosilicate catalysts. Also, by modifying alumina with silica, it was observed that the surface acidity of aluminosilicate catalysts increased with increasing in silica loading. The sample with 6 wt% silica loading has exhibited the best conversion without any by-product.

Keywords: Methanol; Dehydration; Dimethyl ether; Solid-acid catalysts

1. Introduction

Air pollution is one of the most serious environmental problems all over the world. Since, onboard diesel engines of buses and trucks exhaust a huge amount of NO_x and particulates, a clean alternative fuel is desired [1]. In recent years, dimethyl ether (DME), which is now used as a raw material for making chemicals and aerosol propellant such as hair spray, shaving cream to replace ozone-destroying chlorofluorocarbons (CFC), has received attention as an LPG alternative, transportation fuel in substitution to diesel and power generation [2–5].

Catalytic dehydration of methanol over solid-acid catalysts offers a potential process for dimethyl ether synthesis. Several catalysts having activity and selectivity for the catalytic conversion of methanol into DME are known, the so called acidic dehydration catalysts [6,7]. From the literature, it can be concluded that the reaction takes place on different solid-acid catalysts such as γ-alumina, modified-alumina with silica and phosphorus, Al_2O_3–B_2O_3 and molecular sieves materials (chabazites, mordenites, SAPOs,...), in a temperature range of 250–400 °C and pressures up to 18 bar [6–10]. Extensive research has been made especially in order

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to find catalysts having higher selectivity for the ether formation and less tendency to coke formation [7]. It has recent been found that if the reaction of methanol dehydration take place on the modified-alumina catalysts with silica, can be caused to reduce the amounts of coking and by-products [5,7].

In the present work, the catalytic dehydration of methanol to DME has been studied over γ-Al_2O_3 and modified-alumina with silica catalysts. The effect of silica on the catalytic activity of γ-Al_2O_3 have been investigated. In addition, we have investigated the correlation of the activity results with surface acid properties of these catalysts. So, we have attempted to characterize the properties of catalysts by surface area measurements, XRD, etc. This work is part of a long-range effort to develop a new know–how for the conversion of methanol to DME at Haldor Topsøe A/S.

2. Experimental

2.1. Material

The starting materials were aluminium nitrate nanohydrate [ANN; $Al(NO_3)_3 \cdot 9H_2O$], tetraethyl orthosilicate [TEOS; $Si(OC_2H_5)_4$], ethanol [C_2H_5OH] and ammonia solution [max. 33% NH_3].

2.2. Catalysts preparation

2.2.1. γ-Al_2O_3

γ-Al_2O_3 (DME-SCAT2) was obtained by the thermal decomposition of the boehmite (γ-AlOOH, DME-SCAT1) precursor at 550 °C for 6 h at heating rate of 2 °C/min. A commercially available catalyst (it has been developed by Haldor Topsøe A/S, DME-FCAT) was used as a reference solid-acid catalyst for the methanol dehydration catalyst.

2.2.2. Aluminosilicates

A series of aluminosilicate catalysts were prepared by varying amount of silica loading (1, 3, 6, 9 and 15 wt%) by co-precipitation (sol–gel) method. All of the samples were prepared at 50 °C. According to previous study on the aluminosilicate catalysts [11,12], in all these experiments the standard preparation conditions were as follows: co-precipitation by the ammonia solution, the precipitant solution was added slowly at a rate of 4 ml/min, the concentration of ANN and TEOS in ethanol is 2 mole/l, H_2O/TEOS = 10, mixing time 1440 min and NH_4OH/C_2H_5OH ratio = 1/3. The mixture was allowed to react in a glass beaker using a magnetic stirrer (IKA, cylindrical shape, 30 mm length) at about 500 rpm at 50 °C for 24 h. After precipitation, the product dried at 110 °C overnight and calcined in air at 650 °C for 6 h at heating rate of 2 °C/min to remove the residual water, ammonia, ammonium nitrate and organic substances. In more detail aluminosilicate catalysts with 1, 3, 6, 9 and 15 wt% silica loading, were applied DME-AlS1, DME-AlS2, DME-AlS3, DME-AlS4 and DME-AlS5, respectively.

2.3. Characterization of the catalysts

BET surface area, pore volume and pore diameter were measured by N_2 adsorption–desorption isotherm at liquid nitrogen temperature using Autosorb-3B (Quantachrome, USA). Prior to the adsorption–desorption measurements, all the samples were degassed at 300 °C in N_2 flow for 16 h.

The XRD pattern of all the calcined samples were recorded on an X-ray diffractometer (X'Pert PRO, Model PW3040/60 console) using Cu Kα monochromatized radiation source and Ni filter in the range 2θ = 5–90°.

Ammonia temperature programmed desorption (NH_3–TPD) experiments in the temperature range 90–850 °C were conducted using a 0.2 g of catalyst (in a fixed-bed quartz microreactor: i.d., 4 mm and length, 200 mm) under 2% NH_3/He gas mixture stream (100 N ml/min) from room temperature up to 500 °C at a heating rate of 10 °C/min. Before all experiments, catalyst sample (0.2 g) were treated in situ for 2 h in a He flow rate of 100 N ml/min while the temperature was raised from room temperature up to 500 °C at a heating rate of 10 °C/min.

TGA pattern was detected by a Haldor Topsøe TGA-HT thermogravimetric analyzer in order to determine proper calcination and phase transformation conditions. The sample was heated from 25 to 950 °C at heating rate 5 °C/min, in flow of 100 N ml/min of helium.

The chemical compositions of catalysts (Al, Si) were determined by an inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin–Elmer, model Optima 3000) and using Ar as plasmogene.

2.4. Catalytic activity

Catalytic activity of all samples for dehydration of methanol to DME were studied at a steady state in a fixed-bed quartz reactor (i.d., 10 mm and length 650 mm) with an on-line GC. All of the experiments were performed at atmospheric pressure, and temperature of 300 °C. Prior to catalytic testing the samples were crushed and then sieved. For each experiment, 0.5 g of the catalyst (grain size 25–50 mesh or 300–710 μm) was loaded to the reactor by packing quartz wool pads at both of ends of catalyst bed. Nitrogen saturated by pure methanol (11% MeOH in N_2) was used as feed, and the gas hourly space velocity (GHSV) was monitored to 15,600 h^{-1} (feed flow rate